

Free-floating drifter for photochemical studies in the water column

Abstract—A free-floating drifter was designed to directly determine in situ photochemical production rates, photolysis rates, and light fluxes in seawater. This drifter consisted of six trays that were suspended in series from a single buoy line. The trays were constructed so that the attached quartz vessels, containing filtered seawater, were exposed to both downwelling and upwelling irradiation. The quartz vessels were sealed at both ends with ribbed TFE Teflon stoppers that permitted multiple subsampling without introduction of a headspace. The free-floating drifter was used to study photochemical processes in antarctic waters. It performed well during 12–15-h deployments, even in rough seas with sustained winds between 15 and 26 m s⁻¹. Although not tested here, the drifter should perform equally well in the study of photochemical processes in freshwater environments.

One of the most problematic aspects of marine photochemistry is quantification of the depth dependence of light fluxes and photochemical processes. However, this information is needed to determine the importance of a photochemical process in the biogeochemical cycle of a compound or element. In previous field studies, photochemical rates have only been determined at the sea surface by using deckboard irradiations. Other than a few modeling efforts, nothing has been done to extend sea-surface rates to depth-dependent rates. Photochemical models have numerous uncertainties associated with them, particularly with respect to quantification of spatial and temporal variations in the light field (Zepp and Cline 1977). We therefore determined in situ photochemical production rates directly in seawater with a free-floating drifter designed for photochemical studies. The design of this drifter and the attached quartz irradiation vessels contain unique features that are described herein.

The irradiation vessels consisted of quartz tubes with ribbed virgin TFE Teflon stoppers at both ends (Fig. 1). The ribs allowed the Teflon stoppers to be flexible so that they could be forced into the quartz tubes without breaking them. The ribs also maintained a gas-tight seal in the quartz tubes. It was determined that the thickness and depth of each rib, as well as the total number of ribs, were critical for proper seating of the Teflon fittings in the quartz tubes. For example, if the ribs were too thin, they buckled and did not seal properly. The quartz vessels were designed so that one Teflon stopper was fixed (Fig. 2) while the other was used as a gas-tight plunger (Fig. 3), thereby allowing multiple subsampling without introduction of headspace into the quartz tube. This adjustable stopper can be attached to a stainless-steel handle (Fig. 3) that allows seawater to be drawn into and out of the quartz tube during filling and subsampling. The handle is removed during drifter deployments. Stoppers were made of 2.5-cm-diam virgin TFE Teflon rod (Curbell Plastics) and fabricated by the machine shop at the college (SUNY, College of Environmental Science and Forestry). The quartz tubing used in this study (20 mm ID × 24 mm OD) was the highest quality available. It was obtained in

122-cm lengths (Chemglass) and then cut to lengths ≤30 cm.

We conducted an experiment with a chemical actinometer developed in our laboratory (Jankowski et al. unpubl.) to determine if sunlight was focused or attenuated by the quartz vessels when they were placed in a water bath and exposed to sunlight. Three quartz vessels were filled with an aqueous solution of 1 mM sodium nitrate (99.995% purity; Aldrich), 1 mM benzoic acid (recrystallized once from water, ACS reagent grade; Fisher Scientific), and 0.845 mM sodium bromide (99.99% purity; Aldrich). The pH of the solution was adjusted to 8.2 with 1 mM sodium bicarbonate (ACS reagent grade; Baker). The quartz vessels and three uncovered Kimax petri dishes (2 cm high, 9 cm diam) containing the same nitrate solution were placed in a shallow, 20°C water bath (with a black base) and exposed to sunlight for 4 h on the rooftop of Baker Laboratory (Syracuse, New York). No significant difference was observed in the OH radical production rate (±95% C.I.) determined in the quartz tubes (0.64 ± 0.09 μM h⁻¹) compared to the petri dishes (0.68 ± 0.07 μM h⁻¹). Based on this result, we concluded that sunlight <340 nm was not focused or attenuated by the quartz glassware in water. Thus, the quartz vessels should provide reasonably accurate rates for photochemical processes in the water column, assuming that other difficulties are not encountered, such as surface-catalyzed reactions on the quartz glass.

The quartz vessels were also tested in a merimictic lake (Green Lake, Fayetteville, New York) to determine if they sealed well. Three quartz vessels containing anoxic (argon-purged), high-purity laboratory water from a Milli-Q system (Millipore) and three vessels containing 10 nM dimethyl sulfide (Aldrich) were placed in a nylon mesh scuba diving bag and lowered to 30 m, which was in the anoxic zone. In this zone, sulfide concentrations are in the mM range (Brunskill and Ludlam 1969). After a 2-h deployment, the quartz vessels were transported back to the laboratory and the water in the quartz vessels was analyzed for hydrogen sulfide and dimethyl sulfide (DMS) by using gas chromatography with flame photometric detection (Kieber et al. 1996). The concentration of DMS remained constant, and no hydrogen sulfide was detected in any of the six quartz vessels, indicating that there was negligible diffusion of these volatile gases into or out of the quartz vessels during the deployment. That the quartz vessels sealed well was confirmed in a recent study of the photochemical formation of dissolved inorganic carbon (DIC) in Jack Lake (Ontario). In this study, no DIC was detected in DIC-free dark controls after they were incubated for ≥6 h in the lake. The DIC of this lake was 1.1 mM carbon and the pH was 8.4 (Kieber et al. unpubl.).

We did not determine photoproduction rates of CO in the quartz vessels. If CO photoproduction is examined using this system, then the influence of the Teflon stoppers on production rates should be tested, as some batches of Teflon have been shown to produce CO when exposed to sunlight.

In situ photochemical production rates were determined

during two cruises in antarctic waters using the free-floating drifter (Kieber and Mopper 1995, 1996). In a typical drifter experiment, the quartz vessels were first rinsed five times with 0.2- μm filtered seawater collected from a depth of 20 m, and then filled with the same filtered seawater (Yocis 1995). Care was taken not to introduce air into the vessels while filling. After the quartz vessels were filled with filter-sterilized seawater and sampled for initial time points, they were fastened to a drifter tray using 24/40 Keck clips (Fisher Scientific) and further secured with bungie cord. Six trays were suspended in series from a drifter buoy, and set at 2, 4, 6, 10, 15 and 20 m (Fig. 4). Two or three quartz vessels were placed at each depth for each photochemical species that was examined (hydrogen peroxide, OH radical, carbonyl compounds). Separate dark controls were wrapped in aluminum foil. The centers of the drifter trays were cut out (140 \times 508 mm) to allow samples to be exposed to both downwelling and upwelling irradiation (Fig. 5). The drifter trays were fabricated by the Antarctic Support Associates aboard the RV *Nathaniel B. Palmer*, just prior to our 1993 cruise in the Weddell-Scotia seas (Kieber and Mopper 1995).

The free-floating drifter was deployed between 0400 and 0600 h (local time), just prior to or shortly after sunrise. The drifter was tracked during its deployment with an RFD beacon (LFS Marine Supply). While the drifter was in the water, quartz vessels were irradiated in a flow-through seawater bath ($\sim -1^\circ\text{C}$) on the ship's Helo deck to determine sea-surface production rates for each photochemical species that was examined. The drifter was retrieved just prior to sunset at ~ 1930 h. As a control, a separate set of quartz vessels

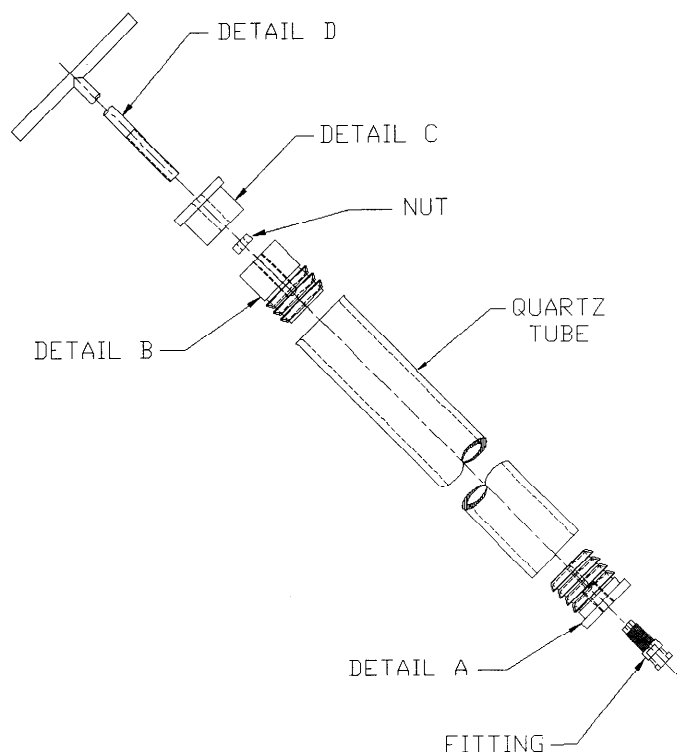


Fig. 1. The quartz irradiation vessel. TFE Teflon plug with a polypropylene luer fitting (detail A), TFE Teflon plunger (B), TFE Teflon guide (C), and 316 stainless steel handle (D).

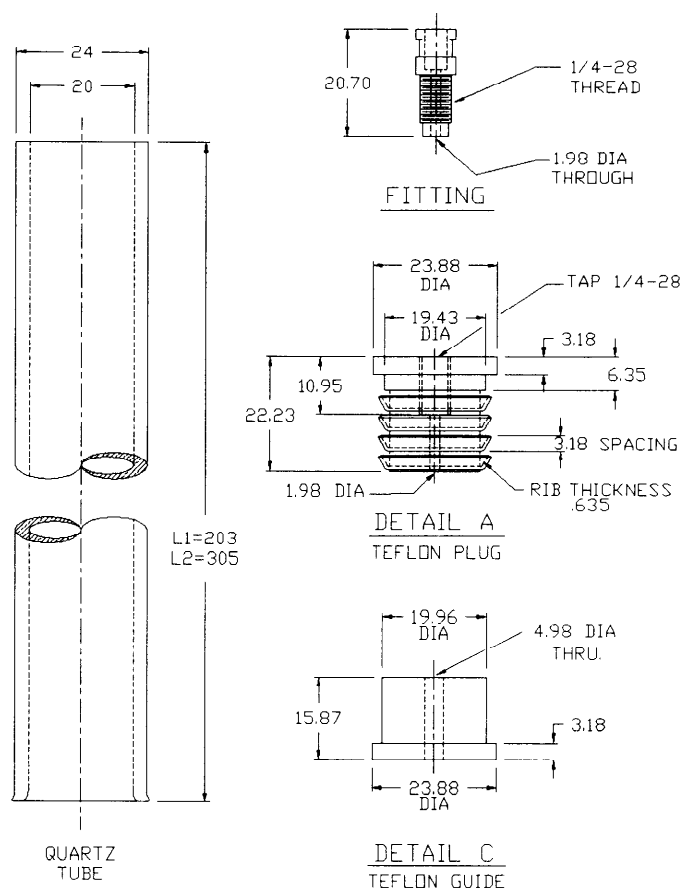


Fig. 2. Metric dimensions (mm) of the quartz tube, as well as detail A of the TFE Teflon plug and detail C of the TFE Teflon guide. The threads and tap are in American Standard units.

was exposed to sunlight only during deployment of the drifter. A similar control was performed during retrieval of the free-floating drifter. This deployment (retrieval) control accounted for photochemical production that occurred during ship operations to assure that any production that was observed in the deeper samples was only due to in situ photochemical processes.

During the two cruises, six experiments were successfully performed with the free-floating drifter, without the loss or damage of any of the quartz vessels (even given sustained winds of between 15 and 26 m s^{-1}).

Results for hydrogen peroxide (H_2O_2) are presented as an example of data obtained from the drifter experiments. Photochemical production rates of hydrogen peroxide are given in units of nM h^{-1} because in situ light fluxes were not available. Note that rates reported here are average daytime rates, since they are based on exposure of the quartz vessels to sunlight for the entire day (12–15 h). We observed that the photochemical production of H_2O_2 decreased exponentially with depth in the 1994 cruise at Sta. A (Fig. 6), with maximal rates observed at the sea surface. The 0.2- μm filtered dark controls showed no production or loss of H_2O_2 . Although underwater irradiation data were not available for this station, results from other drifter deployments (Yocis 1995) demonstrated that the exponential decrease in H_2O_2

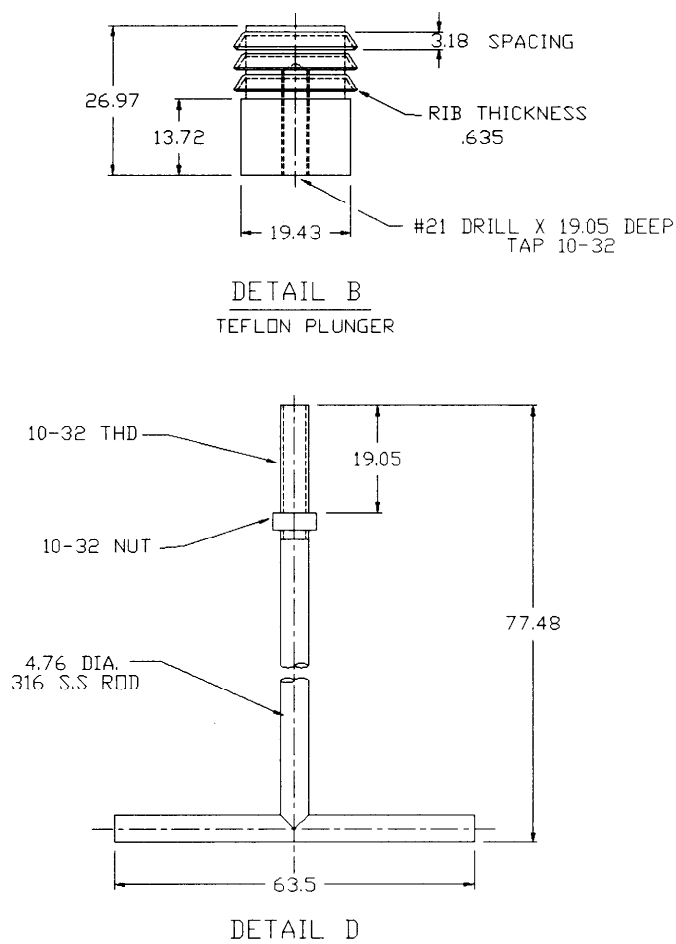


Fig. 3. Detailed metric dimensions (mm) of the TFE Teflon plunger (detail B) and the 316 stainless steel handle (D). The threads and tap are in American Standard units.

production rates paralleled the decrease in UVA (320–400 nm) irradiance with depth, as determined by an underwater spectroradiometer (Biospherical Instruments model PUV 511). The rates depicted in Fig. 6 represent average values for a 13-h deployment of the drifter.

Details of all the drifter results for hydrogen peroxide, the OH radical, and carbonyl compounds will be presented elsewhere in a series of papers dealing with the photochemistry of these compounds in antarctic waters (Yocis 1995; Qian 1996; Qian et al. 1996; Wu 1996).

A limitation of the free-floating drifter is that it cannot provide high-resolution temporal and spatial data for in situ production or photolysis rates. Short drifter deployments (~2 h) may not be long enough to yield measurable rates for the production or photolysis of many species, especially at depths where low UV light levels are encountered (~20 m). Therefore, it may only be possible to determine one to three rates per day at each depth, depending on analytical constraints (e.g. detection limit) and the photochemical reactivity of the water.

One difficulty encountered in the drifter deployments was our inability to measure day-long in situ light fluxes. These data are critical for the determination of light flux-based pho-

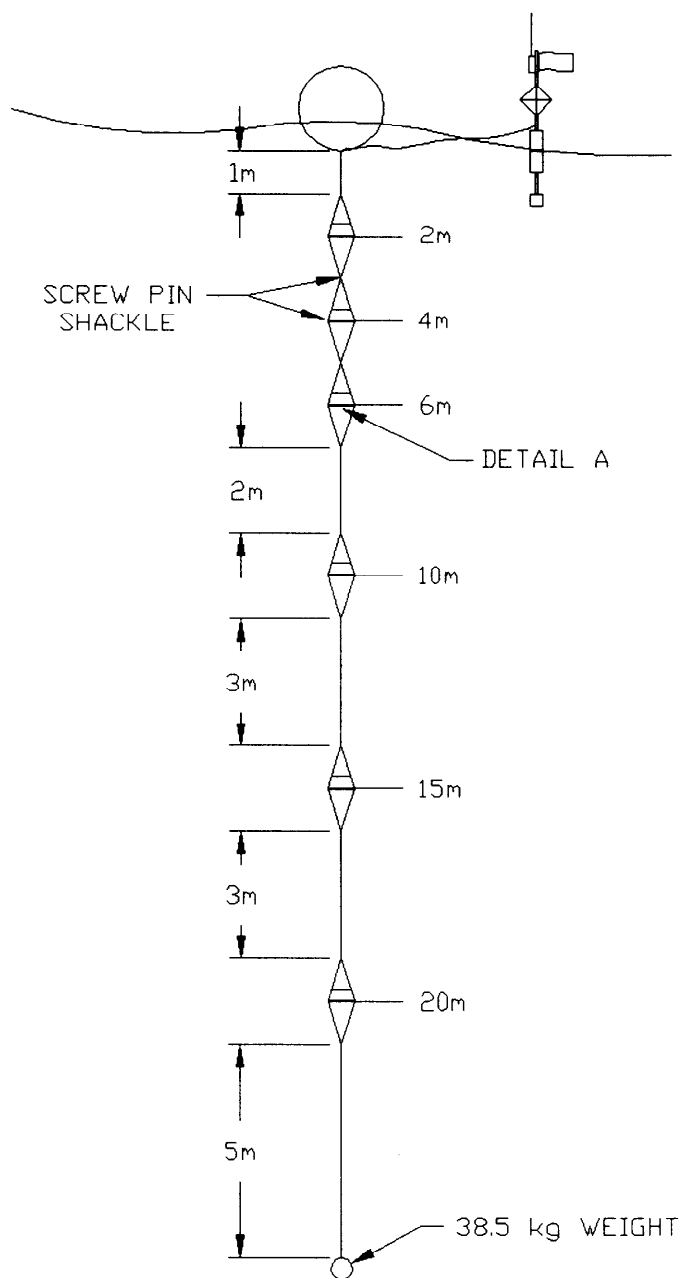


Fig. 4. Free-floating drifter used for in situ photochemical production experiments. The construction of the drifter trays to which the quartz irradiation vessels were attached is shown in Fig. 5. Polypropylene rope and steel shackles were used for all connections.

tochemical production rates as a function of depth in the water column. Otherwise, one has to determine rates as a function of time, as we did, or estimate rates from data for surface and in situ irradiance, DOM absorbance, and photochemical action spectra (if these data are available). To overcome the uncertainties in this latter approach, we are developing highly sensitive UVB and UVA chemical actinometers that permit measurement of these fluxes in the water column (Jankowski et al. unpubl.), even at very low light levels.

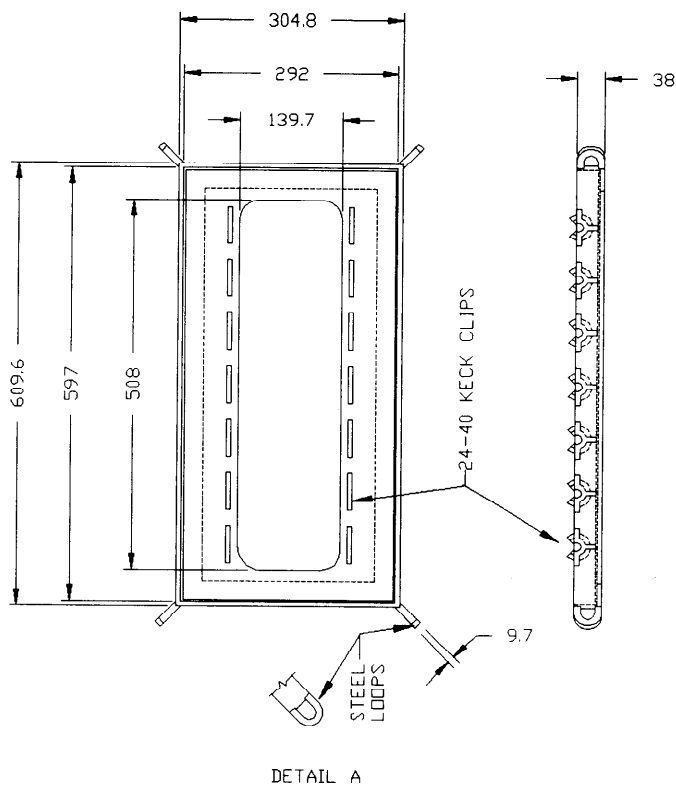


Fig. 5. Cross-sectional view of a drifter tray. Dimensions are in metric units (mm). The drifter trays were constructed out of steel and painted black with an epoxy paint. The Keck clips were fastened to the tray with stainless steel screws.

Although the drifter and quartz vessels were designed for photochemical studies in marine systems, this system should work well in freshwater environments. However, in many freshwater systems, the attenuation of UV in the water column is very rapid (Williamson et al. 1996) so that it would not be feasible to suspend the trays in series along a single buoy line. For freshwater, the drifter trays can be suspended in parallel to each other, similar to the freshwater set up designed by Lindell (1996). In this configuration, the trays will not shade each other. This approach worked well in a photochemical study conducted during July 1996 in Jack Lake, Ontario (Kieber et al. unpubl.).

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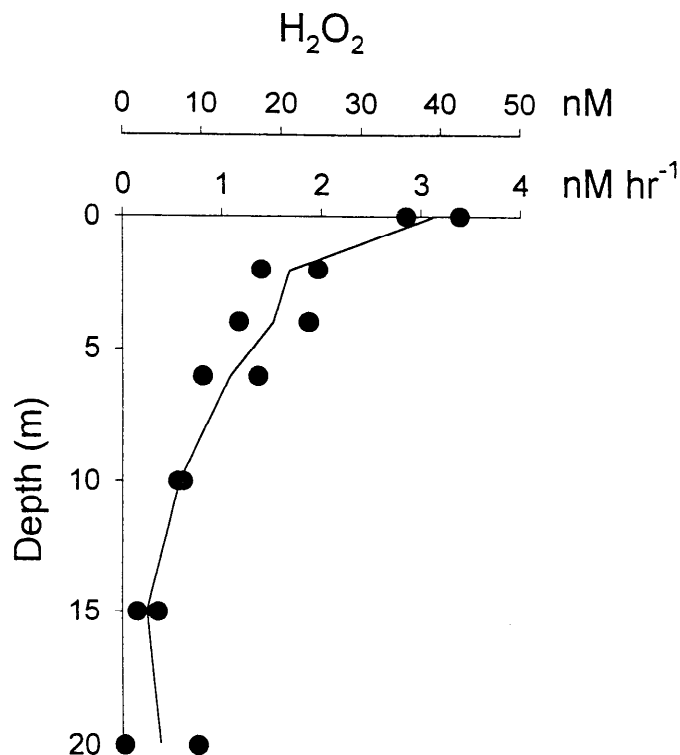


Fig. 6. The photochemical production rate of hydrogen peroxide (●) as a function of depth from the drifter deployment at sta. A on day of the year 345 during the 1994 cruise aboard the RV *Polar Duke*. Sta. A was an open ocean station (64°36'S, 65°18'W) located off the western coast of the Antarctic Peninsula (Yocis 1995). At each depth, the total daytime production of hydrogen peroxide was divided by 13 h to yield the production rate. The solid line represents a plot of the average of the data at each depth.

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